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1,107,495

COMPLETE SPECIFICATION.

Process for Regenerating Palladium Carrier Catalysts for Use in the Manufacture of Vinyl Acetate.

We, KNAPSACK AKTIENGESellschaft, a body corporate organised under the laws of Germany, of 5033 Knapsack bei Koln, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that vinyl acetate can be prepared from ethylene, acetic acid, and oxygen or air in the gaseous phase in contact with a catalyst formed of silica gel, aluminum oxide, pumice, asbestos, active carbon or similar substances as the carrier, and of metallic palladium, which may be used in combination with activating elements, as the active catalyst constituent. These catalysts are very costly, and it is therefore of outstanding commercial significance that they produce good space/time yields and that their activity dies down but fairly slowly. However, these catalysts, too, require to be regenerated from time to time, the regeneration being intended to restore their initially high space/time yields.

The present invention provides a process for regenerating a catalyst which has been used in the manufacture of vinyl acetate, the catalyst containing metallic palladium and, if desired, copper, silver, gold, ruthenium, rhodium, osmium, iridium or platinum, deposited on a silicic acid (SiO_2) carrier, wherein the catalyst to be regenerated is thoroughly washed first with aqueous ammonia having a strength of 1 to 25% and thereafter with water, the washed catalyst is impregnated with an aqueous alkali metal acetate solution having a strength of 1 to 30%, preferably about 10%, the solution is decanted, and the catalyst mass is dried at a temperature of about 50 to 70°C under reduced pressure. The aqueous

ammonia can be used in admixture with 0.01 to 5% by weight, preferably with about 0.1% by weight, hydrazine hydrate.

The regeneration disclosed in the present invention is especially advantageous when the catalysts, owing to excessively long operation periods, are found to contain increased proportions of organic products, or when the catalysts have been repeatedly regenerated by chlorinating them at room temperature and thereafter reducing them by means of hydrazine hydrate. The organic products which poison the catalyst are insoluble in most of the customary solvents, e.g. in dilute acetic acid or acetone. These troublesome compounds cannot be removed completely by chlorination of the catalyst followed by reduction with hydrazine hydrate, though the wash water for washing the catalyst so treated is found to contain chlorinated organic compounds. In the present invention, wherein aqueous ammonia (1 to 25% solution of NH_3 in water) is the wash water, most of the organic compounds are unexpectedly found to dissolve in the ammoniacal solution, which undergoes brown coloration; the fact that the organic compounds dissolve therein appears to indicate that they have an acid nature. In addition to the ammonia, a small amount of hydrazine should conveniently be added to the wash water in order to avoid even slight losses of noble metals.

Catalysts with an initial activity producing a vinyl acetate-space/time yield of about 110 grams/hr per liter of catalyst are found after prolonged operation to be completely inactive and to produce then no more than at most 5 grams/hr vinyl acetate per liter of catalyst. When regenerated in accordance with the present invention, they are found to have again an activity of up

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to 70 grams/hr vinyl acetate per liter of catalyst. It is even more advantageous not to allow the catalyst activity to drop so seriously, but to regenerate the catalyst more frequently by means of ammonia, because this enables the initially high activity of the catalyst to be practically conserved. Percentages referred to throughout are by weight.

10 EXAMPLE:

1 kg silicic acid in the form of strands 3 mm wide was mixed with an aqueous solution containing 10.7 grams palladium in the form of PdCl_2 and 9 grams gold in the form of $\text{H[AuCl}_4]$, and thoroughly impregnated. The whole was dried then with agitation in order uniformly to distribute the noble metal salts on the carrier. The dry mass was slowly introduced at 40°C into a 3% solution of hydrazine hydrate. The palladium chloride and the chlorauric acid immediately underwent reduction which was accompanied by the evolution of nitrogen. Once the reduction was complete, supernatant water was poured off, the whole was after-washed with distilled water, and the moist catalyst was introduced into an about 10% solution of sodium acetate. Excess sodium acetate solution was decanted, and the catalyst was dried at 60°C *in vacuo*. The catalyst so prepared contained 1.03% by weight Pd, 0.86% by weight Au and 1.8% by weight Na in the form of CH_3COONa . The gold content of the catalyst was about 31 atom percent, referred to the gram atoms palladium plus gold. The catalyst was ready for use in the absence of any further treatment.

350 cc of the catalyst mass so prepared were placed into an 18/8 chrome-nickel steel tube having an internal diameter of 25 mm, in which was placed a chrome-nickel steel core tube which had an external diameter of 14 mm and was intended to receive thermo-resistors for temperature determination, and the catalyst mass was maintained at 170°C by gentle heating of the tube. A gas mixture formed of 120 grams acetic acid, 90 normal liters ethylene and 65 normal liters air was caused then, under a pressure of 6 atmospheres absolute, to travel through the tube maintained in upright position. The gas mixture leaving the reaction tube was cooled down to -70°C to remove condensable matter, and the condensed matter was analyzed by distilling it. The catalyst so made produced

vinyl acetate in a space/time yield of 110 to 120 grams per liter of catalyst per hour.

After an operation period of 2 months, the activity of the catalyst was found to have dropped to 3 to 5 grams/hr vinyl acetate per liter of catalyst. The inactive catalyst was washed with a 5% aqueous solution of ammonia containing about 0.1% hydrazine hydrate. The catalyst was thereby freed from organic compounds while the wash water simultaneously underwent marked brown coloration. The catalyst was thoroughly after-washed with water and introduced into a 10% aqueous solution of sodium acetate. The solution was decanted after about 1 hour and the catalyst was dried at 60°C *in vacuo*. The activity which had dropped to 2 to 5 grams/hr vinyl acetate per liter of catalyst was found to have increased to 50 grams/hr.

WHAT WE CLAIM IS:—

1. A process for regenerating a catalyst which has been used in the manufacture of vinyl acetate, the catalyst containing metallic palladium and, if desired, copper, silver, gold, ruthenium, rhodium, osmium, iridium or platinum deposited on silicic acid (SiO_2) as the carrier, wherein the catalyst to be regenerated is thoroughly washed first with aqueous ammonia having a strength of 1 to 25% and thereafter with water, the washed catalyst is impregnated with an aqueous alkali metal acetate solution having a strength of 1 to 30%, preferably about 10%, the solution is decanted and the catalyst mass is dried at about 50 to 70°C under reduced pressure.

2. A process as claimed in claim 1, wherein the aqueous ammonia is used in admixture with 0.01 to 0.5% by weight, preferably with about 0.1% by weight, hydrazine hydrate.

3. A process for regenerating a catalyst which has been used in the manufacture of vinyl acetate conducted substantially as described in the Example herein.

4. Regenerated catalysts for use in the manufacture of vinyl acetate whenever obtained by a process as claimed in any one of claims 1 to 3.

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